

Kinetics of the Anation of Aquadiethylenetriamine-platinum(II) Ions

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Received October 1, 1979

Extensive studies [1, 2] of the kinetics of platinum(II) complexes have shown that a two term rate law prevails, i.e. $k_{\text{obs}} = k_1 + k_2[Y]$. The k_2 term is generally accepted as involving the associative, bimolecular attack of nucleophile Y on the substrate, whereas the first-order rate constant, k_1 , is known to involve an associative solvolysis step. The solvolysis is followed by a rapid anation step, the rate constants for which were independently measured by Gray and Olcott [3] for the complex $\text{Pt}(\text{dien})\text{OH}_2^{2+}$ and $Y = \text{Cl}^-$, Br^- , I^- , NO_2^- , SCN^- and pyridine. These rates were indeed found to be faster by a factor of *ca.* 10^3 than the rates for the solvolysis of the corresponding $\text{Pt}(\text{dien})\text{X}^{n+}$ complexes. In addition, competition between a series of nucleophiles and OH^- for substitution in $\text{Pt}(\text{dien})\text{X}^+$, where $X = \text{Cl}$ or Br , clearly demonstrated that the aqua complex is an intermediate in the k_1 -path.

Our interest in the mechanism of such substitution reactions [4, 5] was particularly aroused by the reported finding [3] that the anation of $\text{Pt}(\text{dien})\text{OH}_2^{2+}$ by Cl^- and NO_2^- also follows the same two term rate law. The explanation for the appearance of a k_1 -path was that it stems from a dissociative process [3]. This rather exceptional behavior for a Pt(II) complex has been discussed in a number of articles [1, 2, 6] and lead us to undertake a more detailed study of this system.

The rates of anation were determined using an Aminco stopped-flow spectrophotometer coupled to a Dasar data storage assembly. The complex solution was prepared by allowing a $2 \times 10^{-3} M$ solution of $[\text{Pt}(\text{dien})\text{Cl}]\text{Cl}$ to react to completion with a 20% excess of OH^- . To a solution containing the desired nucleophile, sufficient HClO_4 was added to bring the final pH of the two solutions after mixing to *ca.* 4. The pK_a of $\text{Pt}(\text{dien})\text{OH}_2^{2+}$ was reported [7] to be 6.13 at 25.2 °C and $\mu = 0.1 M$ (NaClO_4). The reactions were studied at five nucleophile concentrations (*viz.* 0.01, 0.025, 0.05, 0.075 and 0.1 M), while the ionic strength was maintained at *ca.* 0.1 M by the addition of NaClO_4 . The plots of k_{obs} versus $[\text{Y}]$, which are shown in Fig. 1, clearly demonstrate that k_{obs} can be adequately represented by $k_2[\text{Y}]$, within experimental error. The values of k_2 are listed in

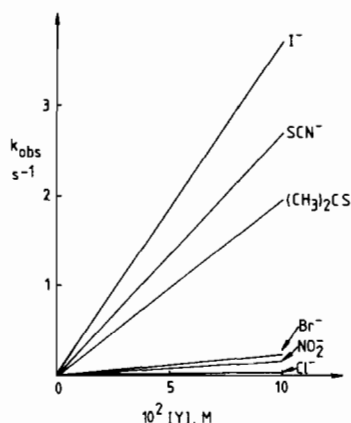


Fig. 1. Plot of k_{obs} versus $[\text{Y}]$ (25 °C; $\mu = 0.1 M$).

TABLE I. Rate Constants for the Anation of $\text{Pt}(\text{dien})\text{OH}_2^{2+}$ at 15 °C and $\mu = 0.1 M$.

Nucleophile	$k_2 M^{-1} s^{-1}$
Cl^-	0.31 ± 0.03
N_3^-	0.40 ± 0.03
NO_2^-	1.60 ± 0.07
Br^-	2.26 ± 0.06
$(\text{CH}_3)_2\text{CS}$	19.8 ± 0.3
SCN^-	27.0 ± 1.0
I^-	37.2 ± 1.2

Table I. We are therefore forced to conclude that the k_1 term observed previously [3] was the direct result of the larger experimental errors incurred, rather than being a real effect, e.g. for $Y = \text{Cl}^-$, $k_1 = (2.4 \pm 1.4) \times 10^{-4} s^{-1}$ and for $Y = \text{NO}_2^-$, $k_1 = (1.9 \pm 1.2) \times 10^{-4} s^{-1}$. Moreover, it is significant that for $Y = \text{Br}^-$ a k_1 value of $(-7 \pm 31) \times 10^{-4} s^{-1}$ was calculated from these earlier results.

The order of decreasing k_2 values was reported [3] to be $\text{I}^- > \text{SCN}^- > \text{Br}^- > \text{Cl}^- > \text{NO}_2^-$, whereas the order of reactivity of the last two nucleophiles is clearly reversed in the present study. This is of particular interest in view of the explanations which were necessary in order to rationalize the apparent anomalous reactivity of NO_2^- over Cl^- towards the aqua complex [8]. By comparison, the trend in the rate constants for substitution in $\text{Pt}(\text{dien})\text{Br}^+$ – also the same for the chloro, iodo and azido analogues [9] – is as follows [9, 10]: thiourea $>$ $\text{SCN}^- >$ $\text{I}^- >$ $\text{Br}^- >$ $\text{N}_3^- >$ $\text{NO}_2^- >$ Cl^- , *cf.* for the anation reactions the order is $\text{I}^- >$ $\text{SCN}^- >$ thiourea $>$ $\text{Br}^- >$ $\text{NO}_2^- >$ $\text{N}_3^- \geq \text{Cl}^-$. The general order of nucleophilic reactivity

for Pt(II) complexes – usually defined in terms of n_{Pt} values – is thiourea $>$ $SCN^- > I^- > Br^- > NO_2^- > N_3^- > Cl^-$ [11]. Although the n_{Pt} values relate to reactions in methanol, they are in good agreement with the order shown above for the substitution reactions of $Pt(dien)X^+$ complexes in aqueous solution. Even taking into account the poorer discriminating ability of $Pt(dien)OH_2^{2+}$ [1], the sequence of anation rate constants still shows a significant disparity, *viz.* thiourea, and to a lesser extent SCN^- , exhibit markedly reduced reactivity towards $Pt(dien)OH_2^{2+}$. This phenomenon may well be the direct result of a decrease in the softness of the doubly charged substrate compared to singly charged and neutral species. For example, the ratio $k_2(\text{thiourea})/k_2(Cl^-)$ for the substrates, *trans*- $Pt(py)_2Cl_2$, $Pt(dien)Br^+$ and $Pt(dien)OH_2^{2+}$ are 13000, 940 and 64, respectively [10, 11]. It is worth mentioning that the effect of charge is not the result of enhanced electrostatic interaction between the more highly charged substrate and the negatively charged Cl^- , because the corresponding ratios of $k_2(\text{pyridine})/k_2(Cl^-)$ show no similar trend, *i.e.* 1.2, 3.8 and 0.34, respectively.

The temperature dependence of the anation of $Pt(dien)OH_2^{2+}$ by Br^- was studied at four temperatures and yielded the activation parameters, $\Delta H^\ddagger = 47.5 \pm 1.7 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -92 + 4 \text{ J K}^{-1} \text{ mol}^{-1}$. The large negative entropy is typical of reactions of Pt(II) complexes and compares closely with the value of $-71 \text{ J K}^{-1} \text{ mol}^{-1}$ reported for the reverse reaction [9], *viz.* the hydrolysis of $Pt(dien)Br^+$. The ΔH^\ddagger of the latter reaction is 82 kJ mol^{-1} [9] emphasizing that the inherent greater stability of bromo complex stems from the stronger Pt–Br bond.

Although these results do not allow us to designate a particular reaction mechanism to the anation reactions of $Pt(dien)OH_2^{2+}$ – and therefore to the corresponding hydrolysis reactions – they are in keeping with both an A and an I_a mechanism. The former is favored in the literature [9] whereby the transition state of higher energy in the reaction profile is envisaged as involving Pt–Y bond formation, while the Pt–OH₂ bond remains intact.

Acknowledgments

The financial support of the Deutsche Forschungsgemeinschaft is gratefully appreciated.

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